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(71) Applicant: KAO CORP

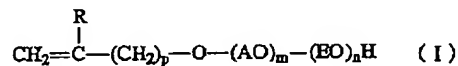
(72) Inventor: IKENAGA NAOYUKI
SAWADA HIROKI
ISHII YASUO(54) REACTIVE SURFACTANT COMPOSITION FOR
EMULSION POLYMERIZATION

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a reactive surfactant composition for emulsion polymerization which gives a polymer emulsion with good polymerization stability, mechanical stability and chemical stability and good water-resistance of polymer film.

SOLUTION: The composition contains an unsaturated compound represented by the formula (1) (wherein R is a hydrogen atom or a methyl group; AO is a 3-18C oxyalkylene group; EO is an oxyethylene group; p is an integer of 2-16; m is an integer of 0-50; n is an integer of 5-200; m (-AO-) groups may be the same or different). The method for producing the emulsion performs the emulsion polymerization by using the composition.

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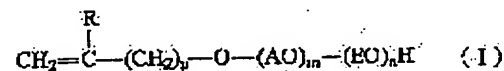
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 (22)Date of filing : 21.09.2000 (72)Inventor : IKENAGA NAOYUKI
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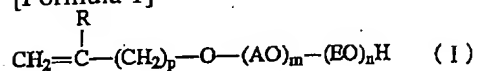
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 CLAIMS

[Claim(s)]

[Claim 1] Formula (I)

[Formula 1]



the inside of a formula, and R -- a hydrogen atom or a methyl group, and AO -- the oxy-alkylene machine of carbon numbers 3-18 -- the number of 0-50 with which in EO an oxyethylene machine and p show the integer of 2-16, and m shows the number of average addition mols of an oxy-alkylene machine, and n are the number of 5-200 which show the number of average addition mols of an oxyethylene machine, and even if m -(AO)-machines are the same, they may differ. The reactive-surface-active-agent constituent for emulsion polymerizations containing the unsaturated compound expressed.

[Claim 2] The reactive-surface-active-agent constituent for emulsion polymerizations containing the unsaturated compound and anionic surfactant which are expressed with a formula (I) according to claim 1.

[Claim 3] The manufacturing method of the polymer emulsion which performs an emulsion polymerization using a reactive-surface-active-agent constituent according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Polymerization stability, mechanical stability, and chemical stability of this invention are good, and it is related with the manufacturing method of the reactive-surface-active-agent constituent for emulsion polymerizations which gives the waterproof good polymer emulsion of a polymer film, and the polymer emulsion using it.

[0002]

[Description of the Prior Art] Fields, such as a paint, an adhesive, paper processing, and textile finishing, or a polymer is separated as it is, and the polymer emulsion obtained according to the emulsion polymerization of vinyl system monomers, such as vinyl acetate and an acrylic ester, is widely used industrially as plastics and rubber. Although various surfactants are used as an emulsifier for emulsion polymerizations, in order to raise the water resistance and adhesive property of a polymer film especially, the surfactant which is generally called reactive surface active agent and which has the unsaturated bond of radical polymerization nature in a molecule is proposed.

[0003] There are anion nature and a nonionic surfactant, like the surfactant of non-reactivity, rather than the reactive surface active agent of non-ionicity, polymerization stability is good to a reactive surface active agent, and the reactive surface active agent of anion nature is widely used for it in the field which needs the water resistance of a film. For the paint use, in order to add an inorganic pigment in large quantities and to hold the stability of an emulsion, the reactive surface active agent of non-ionicity needed to be used, and the reactive-surface-active-agent independence of non-ionicity or the mixed stock of an anionic surfactant and the reactive surface active agent of non-ionicity has been used.

[0004] As a conventional reactive surface active agent of non-ionicity, the butylene oxide of allyl alcohol and the ethyleneoxide addition product, the ethyleneoxide addition product of an undecene acid, etc. are indicated by JP,59-42035,A and JP,59-81302,A. Moreover, the ethyleneoxide addition product of a nonyl phenol and the reactant of allyl glycidyl ether is indicated by JP,62-104802,A. However, the reactive surface active agent of non-ionicity of these former of polymerization stability was inadequate, and it was not a satisfying thing in it.

[0005] The performance required of these reactive surface active agents has polymerization stability, the mechanical stability of the generated polymer emulsion, and good chemical stability, and its copolymerization nature with a monomer is good, and it is excelling in the water resistance of a polymer film. Moreover, it is required that the particle size of an emulsion is small and viscosity is low, that an environmental problem should not occur further, etc. Moreover, it is required in the polymerization method (the pre emulsion method) which emulsifies a monomer, water, and an emulsifier beforehand and is dropped as a monomer emulsion that the stability of a monomer emulsion should also be good. The reactive surface active agent which satisfies all of these performances is not obtained.

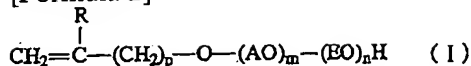
[0006] The technical problem of this invention is to offer the manufacturing method of the reactive-surface-active-agent constituent for emulsion polymerizations with which are satisfied of all the above-mentioned performances, and the polymer emulsion using it.

[0007]

[Means for Solving the Problem] this invention is a formula (I).

[0008]

[Formula 2]



[0009] the inside of a formula, and R -- a hydrogen atom or a methyl group, and AO -- the oxy-alkylene machine of carbon numbers 3-18 -- the number of 0-50 with which in EO an oxyethylene machine and p show the integer of 2-16, and m shows the number of average addition mols of an oxy-alkylene machine, and n are the number of 5-200 which show the number of average addition mols of an oxyethylene machine, and even if m -(AO)-machines are the same, they may differ. They are a reactive-surface-active-agent constituent for emulsion polymerizations containing the unsaturated compound (henceforth an unsaturated compound (I)) expressed, and the manufacturing method of the polymer emulsion which performs an emulsion polymerization using the reactive-surface-active-agent constituent.

[0010]

[Embodiments of the Invention] In a formula (I), from polymerization stability, p is 2-16, is 2-9 preferably, and is 2-6 especially preferably. AO is the oxy-alkylene machine of carbon numbers 3-18, and an oxy-butylene machine or its oxypropylene machine is desirable. Moreover, when adding two or more sorts of alkylene oxide, any of random addition and block addition are sufficient. Moreover, you may combine both addition method. Several m which shows the number of average addition mols of an oxy-alkylene machine is 0-50, and is 0-20 preferably. p and m have the desirable number with which are satisfied of a formula (II), and its number with which are satisfied of a formula (III) is more desirable.

[0011]

$2 \leq \{(\text{carbon number} - 2.8 \text{ of AO}) \times m + p\} \leq 14$ (II) $4 \leq \{(\text{carbon number} - 2.8 \text{ of AO}) \times m + p\} \leq 14$ (III) several n which shows the number of average addition mols of an oxyethylene machine in a formula (I) -- 5-200 from polymerization stability and the pigment miscibility of the obtained polymer emulsion -- it is -- desirable -- 10-60 -- it is 10-40 especially preferably

[0012] An unsaturated compound (I) can be manufactured using a well-known method. For example, it can obtain by adding the alkylene oxide and the ethyleneoxide of carbon numbers 3-18 to the unsaturated alcohol of the carbon numbers 4-19 which have an end unsaturation machine by the well-known method, or adding only an ethyleneoxide.

[0013] As a unsaturated alcohol of the carbon numbers 4-19 which have an end unsaturation machine 3-butene-1-ol, 3-methyl-3-butene-1-ol, 4-pentene-1-ol, 4-methyl-4-pentene-1-ol, 5-hexene-1-ol, 5-methyl-5-hexene-1-ol, 6-heptene-1-ol, 8-nonene-1-ol, 9-decene-1-ol, 10-undecene-1-ol, 11-dodecen-1-ol, 12-tridecenoic-1-ol, 15-hexa decene-1-ol, etc. are mentioned.

[0014] The content of the unsaturated compound in the reactive-surface-active-agent constituent of this invention (I) has 20 - 100 desirable % of the weight, and its 50 - 100 % of the weight is still more desirable.

[0015] As for the reactive-surface-active-agent constituent of this invention, it is desirable to contain an anionic surfactant from a viewpoint of polymerization stability. The anionic surfactant used by this invention has the reactant desirable anionic surfactant which has the unsaturated bond of radical polymerization nature. For example, a sulfo succinate type reactive surface active agent given in JP,58-203960,A and JP,49-46291,B, a sulfate salt type reactive surface active agent given in a pan at JP,62-104802,A and JP,4-53802,A, etc. can be used.

[0016] Moreover, within limits which do not spoil the water resistance of the film manufactured from the emulsion, the anionic surfactant of non-reactivity can also be used, for example, a straight chain alkyl-sulfuric-acid ester salt, straight chain alkylbenzene sulfonates, a polyoxyethylene-alkyl-ether sulfate salt, a polyoxyethylene-alkyl-phenyl-ether sulfate salt, etc. are mentioned.

[0017] When using together an unsaturated compound (I) and an anionic surfactant, from a viewpoint of polymerization stability and chemical stability, as for the mixed ratio, 85 / 15 - 30/70 are desirable at (an unsaturated compound I) / anionic surfactant (weight ratio), and 80 / 20 - 50/50 are still more desirable.

[0018] If the example of the monomer which can perform an emulsion polymerization using the

reactive-surface-active-agent constituent of this invention is given aromatic vinyl monomers, such as styrene, an alpha methyl styrene, and chloro styrene; A methyl acrylate, Acrylic esters, such as an ethyl acrylate and a butyl acrylate; A methyl methacrylate, Methacrylic esters, such as an ethyl methacrylate; A vinyl chloride, vinyl bromide, A halogenation vinyl and halogenation vinylidenes, such as a vinylidene chloride; they are conjugated dienes, such as nitril; butadienes, such as vinyl-esters; acrylonitrile, such as vinyl acetate and a propionic-acid vinyl, and a methacrylonitrile, and an isoprene. Even if it carries out the polymerization of these monomers independently, they may use together and carry out copolymerization of the two or more sorts. The amount of the monomer used has 40 - 60 desirable % of the weight to the whole system.

[0019] the reactive-surface-active-agent constituent of this invention -- the monomer 100 weight section -- receiving -- 0.1 - 20 weight section -- it is preferably desirable 0.2 - 10 weight section and to use in the range of 0.5 - 5 weight section especially

[0020] The radical polymerization initiator used for the emulsion polymerization of this invention has a desirable persulfate, although all can be used and azo system initiators, such as organic peroxide [, such as persulfates, such as potassium persulfate and an ammonium persulfate, a hydrogen peroxide, t-butyl hydroperoxide, benzoyl peroxide, and a cumene hydroperoxide], azobis JISO butyronitrile, 2, and 2-azobis (2-amidinopropane) dihydrochloride, etc. will be mentioned, if used for the usual emulsion polymerization. The initiator of the redox system which furthermore combined reducing agents, such as a sodium sulfite, a Rongalite, and an ascorbic acid, with the peroxidation compound can also be used.

[0021] Although the addition method of a monomer can use a monomer dropping test or the pre emulsion method, polymerization stability to its pre emulsion method is desirable. 1 - 5 hours of a maturing time are [a drop time] desirable for 1 to 8 hours. Although adjusted by the decomposition temperature of an initiator, its 50-90 degrees C are desirable, and when it is especially a persulfate, 70-85 degrees C is desirable [polymerization temperature].

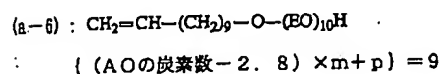
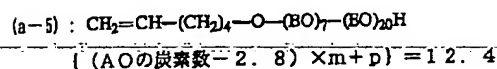
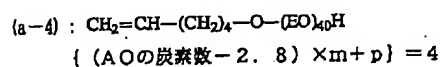
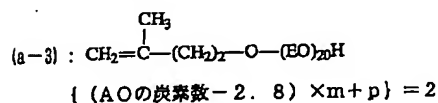
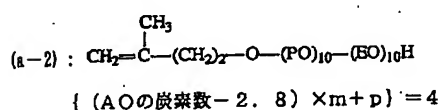
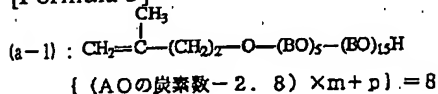
[0022]

[Example] % in an example is weight % unless it mentions specially.

[0023] As the following - (a-1) (a-6) as one to examples 1-10 and example of comparison 8 unsaturated compound (I), and a comparative reactant nonionic surface active agent: As the following - (b-1) (b-5) and an anionic surfactant, using the following - (c-1) (c-2); it blended at a rate shown in Table 1, and this invention and the comparative reactive-surface-active-agent constituent were prepared. The emulsion polymerization was performed by the method shown below using this reactive-surface-active-agent constituent, and the method shown below estimated the performance. A result is shown in Table 1.

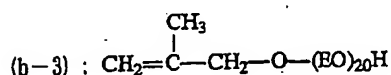
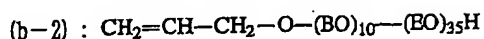
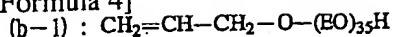
[0024]

[Formula 3]

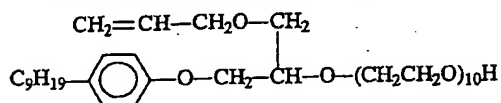


[0025]

[Formula 4]



(b-4) : 特開昭 6 2 - 1 0 4 8 0 2 号に開示の化合物

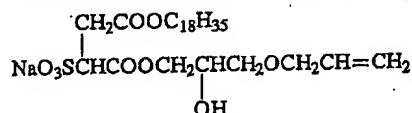


(b-5) : ノニルフェノール・エチレンオキサイド 3 5 モル付加物

[0026]

[Formula 5]

(C-1) : 特開昭 5 8 - 2 0 3 9 6 0 号に開示の化合物



(C-2) : 直鎖アルキル (炭素数 1 2) ベンゼンスルホン酸の Na 塩

[0027] 2.8g of <emulsion-polymerization method> acrylic acids, 136.1g of butyl acrylates, and 136.1g of methyl methacrylates were mixed, and monomer mixture was prepared. 5.5g of reactive-surface-active-agent constituents and 0.275g of potassium persulfate were dissolved in 117.9g of ion exchange water, the above-mentioned monomer mixture was mixed, it emulsified for 5000 r/minx 10 minutes in the homomixer, and the uniform monomer emulsification object was obtained.

[0028] 135.4g of ion exchange water, potassium persulfate 0.25 g, and the 36.3g of the above-mentioned monomer emulsification objects were taught to the separable flask, and it stirred for 15 minutes in the nitrogen air current. Next, the temperature up was put in and carried out to the 80-degree C water bath, stirring in a nitrogen air current. The first stage polymerization during 30 minutes was carried out, and 326.3g of monomer emulsification objects was dropped over 3 hours. The temperature in a flask was kept at 80**2 degrees C in the meantime. It kept at 80 degrees C after the dropping end for 1 hour, and after riping, it cooled to the room temperature and the polymer emulsion was obtained.

[0029] The <performance-evaluation method> (1) polymerization stability polymer emulsion was filtered at the wire gauze made from stainless steel of 200 meshes, and the aggregates adhering to a reactor wall, an impeller, etc. after a polymerization were also collected, and it filtered similarly, it carried out 2-hour dryness and weighing capacity at 26.6kPa and 105 degrees C after rinsing, and the amount of aggregates was calculated. Polymerization stability was expressed with weight % of the aggregate to the total amount of the used monomer.

[0030] (2) Polymer emulsion 50g neutralized with 25% NH3 of mechanical stability water was rotated for 5 minutes on condition that 10kgf(s) and 1000 r/min with the chestnut stable testing machine, the generated aggregate was filtered at the wire gauze made from stainless steel of 200 meshes, and after rinsing a filtration residue, it displayed at 26.6kPa(s) and 105 degrees C by 2-hour dryness and weight [of an aggregate / as opposed to / carry out weighing capacity and / polymer] %.

[0031] (3) Dynamic-light-scattering particle-size measuring device N4 Plus by the mean-particle-diameter coal tar company was used, and the mean particle diameter of the polymer emulsion particle after neutralization was measured.

[0032] (4) The viscosity Brookfield viscometer was used and the viscosity of the polymer emulsion

after neutralization was measured by the temperature of 25 degrees C, and rotational frequency 12 r/min.

[0033] (5) The concentration which an aggregate produces was measured by diluting the polymer emulsion after chemical stability neutralization with ion exchange water to 3% of polymer concentration, and titrating it using 1molL⁻¹ calcium-chloride solution.

[0034] (6) Extended the polymer emulsion after neutralizing on the waterproof slide glass of a polymer film, it was made to dry at 60 degrees C, and the polymer film was created. It was immersed into 25-degree C ion exchange water, and the milkiness situation of a film was evaluated.

O after :1-hour progress -- completely -- after milkiness-less O:1-hour progress -- a little -- milkiness
*:10 - 30 minutes -- milkiness x: -- immediately -- milkiness [0035]

[Table 1]

		反応性界面活性剤組成物			重合安定性 (%)	機械的安定性 (%)	平均粒径 (nm)	粘度 (mPa·s)	化学的安定性 (mmolL ⁻¹)	ポリマーフィルムの耐水性
		(A) 反応性非 イオン界 面活性剤	(B) 陰イオン界 面活性剤	(A)/(B) 重量比						
実施例	1	(a-1)	(c-1)	80/20	0.18	0.09	260	230	>1500	◎
	2	(a-1)	(c-1)	50/50	0.16	0.05	195	1200	720	◎
	3	(a-2)	(c-1)	60/40	0.23	0.13	240	260	1150	○
	4	(a-3)	(c-1)	80/20	0.25	0.12	250	230	>1500	○
	5	(a-3)	(c-1)	67/33	0.21	0.11	235	260	1430	○
	6	(a-4)	(c-1)	80/20	0.20	0.08	240	250	>1500	◎
	7	(a-4)	(c-2)	70/30	0.19	0.07	220	270	>1500	○
	8	(a-5)	(c-1)	80/20	0.14	0.02	220	250	>1500	◎
	9	(a-5)	(c-1)	60/40	0.15	0.05	200	850	>1500	◎
	10	(a-6)	(c-1)	80/20	0.22	0.04	230	255	>1500	◎
比較例	1	なし	(c-1)	—	0.25	0.04	165	1030	20	◎
	2	(b-1)	(c-1)	80/20	2.04	0.22	270	210	>1500	△
	3	(b-1)	(c-1)	50/50	0.58	0.39	260	280	540	△
	4	(b-1)	(c-2)	80/20	1.05	0.45	190	1500	>1500	△
	5	(b-2)	(c-1)	80/20	0.72	0.33	265	230	>1500	△
	6	(b-3)	(c-1)	80/20	0.94	0.28	270	240	>1500	△
	7	(b-4)	(c-1)	80/20	4.33	0.36	230	270	>1500	△
	8	(b-5)	(c-1)	80/20	0.48	0.24	225	260	>1500	△

[0036]

[Effect of the Invention] If the reactive-surface-active-agent constituent of this invention is used for an emulsion polymerization, polymerization stability, mechanical stability, and chemical stability will be good, and a polymer emulsion with the good water resistance of a polymer film will be obtained.

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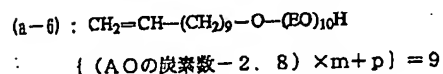
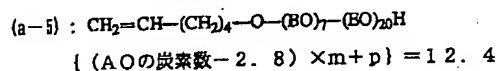
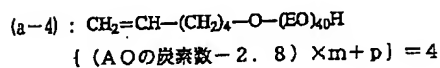
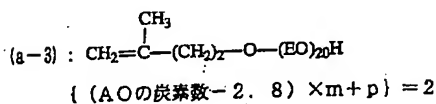
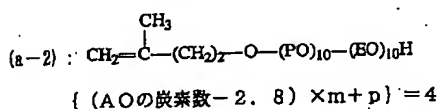
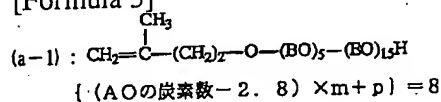
EXAMPLE

[Example] % in an example is weight % unless it mentions specially.

[0023] As the following - (a-1) (a-6) as one to examples 1-10 and example of comparison 8 unsaturated compound (I), and a comparative reactant nonionic surface active agent. As the following - (b-1) (b-5) and an anionic surfactant, using the following - (c-1) (c-2), it blended at a rate shown in Table 1, and this invention and the comparative reactive-surface-active-agent constituent were prepared. The emulsion polymerization was performed by the method shown below using this reactive-surface-active-agent constituent, and the method shown below estimated the performance. A result is shown in Table 1.

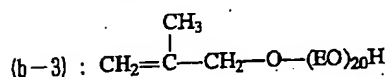
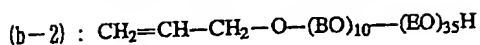
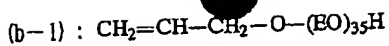
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[Formula 3]

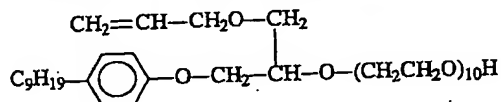


[0025]

[Formula 4]



(b-4) : 特開昭 6 2 - 1 0 4 8 0 2 号に開示の化合物

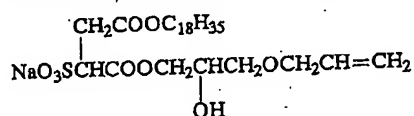


(b-5) : ノニルフェノール・エチレンオキシド 3 5 モル付加物

[0026]

[Formula 5]

(C-1) : 特開昭 5 8 - 2 0 3 9 6 0 号に開示の化合物



(C-2) : 直鎖アルキル (炭素数 1 2) ベンゼンスルホン酸の Na 塩

[0027] 2.8g of <emulsion-polymerization method> acrylic acids, 136.1g of butyl acrylates, and 136.1g of methyl methacrylates were mixed, and monomer mixture was prepared. 5.5g of reactive-surface-active-agent constituents and 0.275g of potassium persulfate were dissolved in 117.9g of ion exchange water, the above-mentioned monomer mixture was mixed, it emulsified for 5000 r/minx 10 minutes in the homomixer, and the uniform monomer emulsification object was obtained.

[0028] 135.4g of ion exchange water, potassium persulfate 0.25 g, and the 36.3g of the above-mentioned monomer emulsification objects were taught to the separable flask, and it stirred for 15 minutes in the nitrogen air current. Next, the temperature up was put in and carried out to the 80-degree C water bath, stirring in a nitrogen air current. The first stage polymerization during 30 minutes was carried out, and 326.3g of monomer emulsification objects was dropped over 3 hours. The temperature in a flask was kept at 80**2 degrees C in the meantime. It kept at 80 degrees C after the dropping end for 1 hour, and after-ripping, it cooled to the room temperature and the polymer emulsion was obtained.

[0029] The <performance-evaluation method> (1) polymerization stability polymer emulsion was filtered at the wire gauze made from stainless steel of 200 meshes, and the aggregates adhering to a reactor wall, an impeller, etc. after a polymerization were also collected, and it filtered similarly, it carried out 2-hour dryness and weighing capacity at 26.6kPa and 105 degrees C after rinsing, and the amount of aggregates was calculated. Polymerization stability was expressed with weight % of the aggregate to the total amount of the used monomer.

[0030] (2) Polymer emulsion 50g neutralized with 25% NH3 of mechanical stability water was rotated for 5 minutes on condition that 10kgf(s) and 1000 r/min with the chestnut stable testing machine, the generated aggregate was filtered at the wire gauze made from stainless steel of 200 meshes, and after rinsing a filtration residue, it displayed at 26.6kPa(s) and 105 degrees C by 2-hour dryness and weight [of an aggregate / as opposed to / carry out weighing capacity and / polymer] %.

[0031] (3) Dynamic-light-scattering particle-size measuring device N4 Plus by the mean-particle-diameter coal tar company was used, and the mean particle diameter of the polymer emulsion particle after neutralization was measured.

[0032] (4) The viscosity Brookfield-viscometer-was-used-and-the viscosity of the polymer emulsion after neutralization was measured by the temperature of 25 degrees C, and rotational frequency 12 r/min.

[0033] (5) The concentration which an aggregate produces was measured by diluting the polymer

emulsion after chemical stability neutralization with ion exchange water to 3% of polymer concentration, and titrating it using 1molL⁻¹ calcium-chloride solution.

[0034] (6) Extended the polymer emulsion after neutralizing on the waterproof slide glass of a polymer film, it was made to dry at 60 degrees C, and the polymer film was created. It was immersed into 25-degree C ion exchange water, and the milkiness situation of a film was evaluated.

O after : 1-hour progress -- completely -- after milkiness-less O: 1-hour progress -- a little -- milkiness
*: 10 - 30 minutes -- milkiness x: -- immediately -- milkiness [0035]

[Table 1]

Table 1

		反応性界面活性剤組成物			重合安定性 (%)	機械的安定性 (%)	平均粒径 (nm)	粘度 (mPa・s)	化学的安定性 (mmolL ⁻¹)	ポリマーフィルムの耐水性
		(A) 反応性非イオン界面活性剤	(B) 陰イオン界面活性剤	(A)/(B) 重量比						
実施例	1	(a-1)	(c-1)	80/20	0.18	0.09	260	230	>1500	◎
	2	(a-1)	(c-1)	50/50	0.16	0.05	195	1200	720	◎
	3	(a-2)	(c-1)	60/40	0.23	0.13	240	260	1150	○
	4	(a-3)	(c-1)	80/20	0.25	0.12	250	230	>1500	○
	5	(a-3)	(c-1)	67/33	0.21	0.11	235	260	1430	○
	6	(a-4)	(c-1)	80/20	0.20	0.08	240	250	>1500	◎
	7	(a-4)	(c-2)	70/30	0.19	0.07	220	270	>1500	○
	8	(a-5)	(c-1)	80/20	0.14	0.02	220	250	>1500	◎
	9	(a-5)	(c-1)	60/40	0.15	0.05	200	850	>1500	◎
	10	(a-6)	(c-1)	80/20	0.22	0.04	230	255	>1500	◎
比較例	1	なし	(c-1)	—	0.25	0.04	165	1030	20	◎
	2	(b-1)	(c-1)	80/20	2.04	0.22	270	210	>1500	△
	3	(b-1)	(c-1)	50/50	0.58	0.39	260	280	540	△
	4	(b-1)	(c-2)	80/20	1.05	0.45	180	1500	>1500	△
	5	(b-2)	(c-1)	80/20	0.72	0.33	265	230	>1500	△
	6	(b-3)	(c-1)	80/20	0.94	0.28	270	240	>1500	△
	7	(b-4)	(c-1)	80/20	4.33	0.36	230	270	>1500	△
	8	(b-5)	(c-1)	80/20	0.48	0.24	225	260	>1500	△

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TECHNICAL PROBLEM

[Description of the Prior Art] Fields, such as a paint, an adhesive, paper processing, and textile finishing, or a polymer is separated as it is, and the polymer emulsion obtained according to the emulsion polymerization of vinyl system monomers, such as vinyl acetate and an acrylic ester, is widely used industrially as plastics and rubber. Although various surfactants are used as an emulsifier for emulsion polymerizations, in order to raise the water resistance and adhesive property of a polymer film especially, the surfactant which is generally called reactive surface active agent and which has the unsaturated bond of radical polymerization nature in a molecule is proposed.

[0003] There are anion nature and a nonionic surfactant, like the surfactant of non-reactivity, rather than the reactive surface active agent of non-ionicity, polymerization stability is good to a reactive surface active agent, and the reactive surface active agent of anion nature is widely used for it in the field which needs the water resistance of a film. For the paint use, in order to add an inorganic pigment in large quantities and to hold the stability of an emulsion, the reactive surface active agent of non-ionicity needed to be used, and the reactive-surface-active-agent independence of non-ionicity or the mixed stock of an anionic surfactant and the reactive surface active agent of non-ionicity has been used.

[0004] As a conventional reactive surface active agent of non-ionicity, the butylene oxide of allyl alcohol and the ethyleneoxide addition product, the ethyleneoxide addition product of an undecene acid, etc. are indicated by JP,59-42035,A and JP,59-81302,A. Moreover, the ethyleneoxide addition product of a nonyl phenol and the reactant of allyl glycidyl ether is indicated by JP,62-104802,A. However, the reactive surface active agent of non-ionicity of these former of polymerization stability was inadequate, and it was not a satisfying thing in it.

[0005] The performance required of these reactive surface active agents has polymerization stability, the mechanical stability of the generated polymer emulsion, and good chemical stability, and its copolymerization nature with a monomer is good, and it is excelling in the water resistance of a polymer film. Moreover, it is required that the particle size of an emulsion is small and viscosity is low, that an environmental problem should not occur further, etc. Moreover, it is required in the polymerization method (the pre emulsion method) which emulsifies a monomer, water, and an emulsifier beforehand and is dropped as a monomer emulsion that the stability of a monomer emulsion should also be good. The reactive surface active agent which satisfies all of these performances is not obtained.

[0006] The technical problem of this invention is to offer the manufacturing method of the reactive-surface-active-agent constituent for emulsion polymerizations with which are satisfied of all the above-mentioned performances, and the polymer emulsion using it.

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